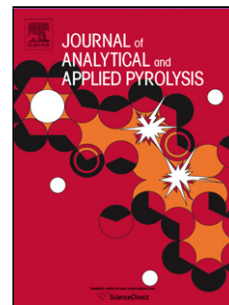


## Accepted Manuscript

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# **Influence of pyrolysis temperature and holding time on properties of biochar derived from medicinal herb (radix isatidis) residue and its effect on soil CO<sub>2</sub> emission**

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## **Abstract**

Radix isatidis is a wide-spread medicinal herb in China. The boiled radix isatidis residue contains considerable quantities of cellulose, hemicellulose, and lignin that could be used as feedstock for biochar production. This study aims to investigate the influence of pyrolysis temperature and holding time on biochar properties as well as the effect of biochar on soil CO<sub>2</sub> emission in southern China. The biochar was prepared using pyrolysis over a temperature range of 300 °C to 700 °C and a holding time span of 10 min to 180 min. The incubation experiment of soil incorporated with biochar lasted for 46 days. Increasing temperature and prolonging holding time were found to reduce the volatile matter content, strengthen the carbon enrichment, and grow aromatic structure, producing alkaline biochar that has weak surface polarity, high specific surface area and extensively porous structures. The effect of biochar on soil CO<sub>2</sub> emission in southern China lays in the combined actions of biochar properties, especially of volatile matter, porous structure, and pH. Increasing temperature and extending holding time may convert the positive effect into a negative effect and reduce soil CO<sub>2</sub> emission.

Key words: pyrolysis, biochar, radix isatidis, soil CO<sub>2</sub> emission

## **1. Introduction**

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Thermal conversion of biomass in the absence of oxygen (i.e., pyrolysis) yields liquid (bio-oil), gaseous (syngas), and solid products [1]. The solid products have historical applications dating back to the dawn of human civilization [2]. A new name, biochar, has recently been used to describe the solid products returned to soil for soil quality improvement [3, 4] and carbon sequestration benefits [5, 6]. These biochar benefits are closely related to its physical and chemical properties, which mainly depend on the biochar feedstock and pyrolysis conditions such as temperature and holding time. For example, studies on the biochar derived from cottonseed hull indicated that elevating temperature could increase the specific surface area [7] and reduce biochar acidity [8, 9]. Furthermore, higher cation exchange capacity (CEC) has been observed in biochar prepared with poultry litter, peanut hull and pine chip under low pyrolysis temperature [4]. For biochar derived from hardwood, softwood, grasses and sludge, researches have shown that raising pyrolysis temperature could accelerate organism decomposition and carbonization, which further increase ash and fixed carbon contents in biochar [10].

In addition, biochar also affects soil CO<sub>2</sub> emission when returned to soil as amendment. Owing to the inconsistency of biochar type (different feedstock and production conditions) and soil type (different microorganism and aggregation status, organic matter, nutrient and water contents, etc.), previous studies showed the priming effect was inconsistent, which might be positive, insignificant, or even negative, on soil organic carbon degradation [11-14]. A case in point was a comparative study using 16 chars and two soil types, approximately a third increased, a third decreased, and a third had no effect on soil organic carbon respiration [15].

*Radix isatidis* is a medicinal herb wide-spread in China. The boiled *radix isatidis* residue, according to our experiment, contains abundant cellulose, hemicellulose, and lignin (28.8% cellulose, 22.6% hemicellulose, and 36.5% lignin, respectively) like other biomasses, suggesting that the feedstock may be a suitable source for biochar production although no such use have been considered previously. The aims of this study were to evaluate the influence of pyrolysis temperature and holding time on the properties such as the composition, pH, porous structure, and spectral characteristics

of biochar derived from boiled radix isatidis residue, as well as the soil CO<sub>2</sub> emission of southern China soil amended with the biochar produced under various conditions.

## 2. Materials and methods

### 2.1. Biochar feedstock and soil

Biochar feedstock was boiled radix isatidis residue, a medicinal herb residue collected from Chaozhou yikang herbal pieces limited company (116°6'69"E and 23°6'75"N) in Chaozhou, Guangdong Province. The feedstock was dried overnight at 105 °C in a convection laboratory oven and then was cut into 1 mm to 2 mm fine particles with a compact edge-type pulverizer. Thereafter, the feedstock particles were stored in airtight plastic bags until pyrolysis. The ultimate and proximate analyses of the feedstock were shown in Tables 1 and 2. Volatile matter and ash contents were determined using a slightly modified version of the ASTM (American Society for Testing Material) method (D-1762-84). Approximately 1.0 g of non-ground samples that had been kept in a drying oven for at least 3 h at 105 °C and cooled in a desiccator was weighed into preweighed ceramic crucibles. The volatile matter content was determined as weight loss after combustion with a loose ceramic cap under 900 °C for 7 min. The ash content was determined as weight loss after combustion under 815 °C for 6 h with no ceramic cap. The sample weight was measured after cooling in a desiccator for 1 h. Fixed carbon was calculated based on the difference by assuming a composition of fixed carbon, volatile matter, and ash (no moisture).

The soil for laboratory studies was sampled from an experimental farmland in Guangzhou, Guangdong Province (113°6'69"E and 23°1'65"N). The site was farmed for rice production. The soil at the site is a Typic Plinthudult (Ultisol) as classified by the USDA (United States Department of Agriculture) Soil Taxonomy [16], containing approximately 21% sand, 53% silt, 26% clay with a pH (1:1 H<sub>2</sub>O) of 6.3 to 6.6, and 2.5% organic carbon. Surface soil (0 cm to 20 cm) was collected after rice harvest, sieved to <2 mm, and homogenized for the incubation study. The soil was collected

within one month of initiating soil incubation to reduce the effect of storage on microbial assessment [17].

## 2.2. Biochar production

100  $\pm$  1.0 g of feedstock sample were used to produce biochar with a horizontal quartz reactor (60 cm length  $\times$  5 cm i.d.) placed in an electrical laboratory furnace. Approximately 1000 mL min<sup>-1</sup> flow rate of purified nitrogen (99.999%) was maintained throughout each pyrolysis experiment for an inert oxygen-free atmosphere. Therefore, the internal pressure of the horizontal quartz reactor was consistent with the atmospheric pressure. The heating rate was 10 °C min<sup>-1</sup>, and the desired temperature was 300, 500, and 700 °C respectively. The procedure for each pyrolysis experiment was described below.

The feedstock sample was loaded in the horizontal quartz reactor first. Then the horizontal quartz reactor was placed in the electrical laboratory furnace, and nitrogen flow was opened. The electrical laboratory furnace was heated from the ambient temperature (25 °C) to the desired temperature, then the horizontal quartz reactor was maintained under the desired temperature for 10, 90, and 180 min, respectively. With each experiment processing, the condensable matter (bio-oil and water) was quenched and collected in a flask, whereas the residual gaseous material and nitrogen was discharged into the atmosphere after being absorbed and purified. When the pyrolysis was completed, the horizontal quartz reactor was removed from the electrical laboratory furnace immediately, and the electrical laboratory furnace was switched off, then the biochar was recovered and the nitrogen flow was closed until the reactor temperature was the same as the ambient temperature.

## 2.3. Biochar properties analysis

After being ground in a silica mortar, approximately 5 mg of sample was used for carbon, nitrogen, and hydrogen determination in an elemental analyzer (vario EL cube, Germany). The oxygen content was calculated based on difference by assuming a

composition of carbon, nitrogen, hydrogen, oxygen, and ash. All samples were analyzed in triplicate.

The biochar pH was measured in the supernatant of aqueous solution (solid-water ratio was 1:5) with a digital pH meter (PHB-4, lei-ci, China). Pore structures of biochars were characterized by nitrogen adsorption at 77 K with an automated surface area and pore size analyzer (Quanta chrome SI-MP-10). The specific surface area was taken from adsorption isotherms using the BET (Brunauer, Emmett and Teller) equation. The Dubinin–Astakhov (DA) method was used to calculate the micropore and mesopore volume [18]. The total volume was estimated by converting the amount of N<sub>2</sub> gas adsorbed under a relative pressure of 0.99 to the liquid volume of the adsorbate (N<sub>2</sub>). To obtain the FTIR spectra, ground biochar was mixed with KBr to 0.1 wt.% and was pressed into pellets for Fourier transform infrared spectroscopy (FTIR, Nicolet 6700). The spectra were obtained by 32 scans of the sample at a resolution of 4 cm<sup>-1</sup> and an interval of 1 cm<sup>-1</sup>. The resulting spectra were normalized to the highest peak in the fingerprint region between 4000 and 500 cm<sup>-1</sup>.

#### 2.4. Incubation of biochar amended soil

Each biochar was incorporated, in triplicate, into 50 g of soil with a ratio of 1% by dry weight and a bulk density of 1.2 mg m<sup>-3</sup> (similar to the field condition). The soil without biochar was treated as control. Each soil sample was placed into a 500 mL airtight opaque brown bottle and incubated in a dark room at 25 ± 2 °C for 46 d. During incubation, the soil water content was maintained at 0.16 mL g<sup>-1</sup> (equivalent to 40% of field capacity) through daily adjustment based on weight for better CO<sub>2</sub> flux. To determine the soil CO<sub>2</sub> emission in control and the sample incorporated with biochar, the evolved C-CO<sub>2</sub> was trapped in 0.20 mol L<sup>-1</sup> NaOH solution. The bound CO<sub>2</sub> was determined during incubation by titration with 0.10 mol L<sup>-1</sup> HCl solution followed by the addition of 1.0 mol L<sup>-1</sup> BaCl<sub>2</sub> [19].

#### 2.5. Statistic analysis

ANOVA was applied to test the effects of temperature and holding time on the properties of feedstock and biochar as well as the amount of CO<sub>2</sub> emission in the control and the soil incorporated with biochar. (The criterion for statistical significance was set as  $P < 0.05$ ) test while assessing the differences among the means of three replications.

### 3. Results and discussion

#### 3.1. Ultimate analysis

The absolute and relative contents of carbon, oxygen, and hydrogen were shown in Table 1. The depletion of carbon, oxygen, and hydrogen during pyrolysis reduced the absolute contents of these elements in biochar than in feedstock. However, the relative carbon contents in biochar were higher than that in feedstock and the contents were increasing with increasing temperature and extended holding time. This indicates that carbon was enriched with temperature rise, which is consistent with a previous report where carbon in pitch pine biochar was enriched when the temperature increased from 300 °C to 500 °C [20]. As extending holding time was also shown to intensify carbon content, a carbon-rich biochar could be achieved by pyrolysis with higher temperature and longer holding time.

As showed in Fig. 1, feedstock O/C and H/C atomic ratio were 0.63 and 1.70, respectively, suggesting abundant oxygen and hydrogen contents, which were similar to other biomasses [21]. In addition, biochar produced at a higher temperature [22] with longer holding time has a lower O/C atomic ratio and H/C atomic ratio, suggesting the depletion of oxygen and hydrogen and enrichment of carbon. Moreover, the lower H/C indicates that the biochar produced with higher temperature and longer holding time becomes more aromatic [23], it may exist stably in soil.

#### Table 1

Absolute and relative contents of carbon, oxygen, and hydrogen in feedstock and biochars prepared with various temperatures and holding time.

	Temperature (°C)	Holding time (min)	Relative content <sup>a</sup>			Absolute content		
			C (%)	H (%)	O (%)	C (g)	H (g)	O (g)
Feedstock	-	-	42.85	6.06	36.03	42.85	6.06	36.03
			±2.85	±0.065	±6.03	±2.85	±0.065	±6.03
		10	54.85	4.55	19.98	42.69	3.24	14.25
			±4.85	±0.555	±9.98	±2.69	±0.249	±4.25
		90	56.28	4.55	17.37	37.92	2.12	6.81
			±6.28	±0.558	±7.37	±7.92	±0.122	±0.812
		180	58.01	4.56	13.93	35.82	1.96	4.37
			±8.01	±0.561	±3.93	±5.82	±0.962	±0.372
		10	60.84	3.07	14.97	37.36	1.89	9.20
			±0.84	±0.074	±4.97	±7.36	±0.896	±0.206
Biochar	500	90	64.08	2.77	10.70	36.73	1.59	6.13
			±4.08	±0.778	±0.70	±6.73	±0.593	±0.133
		180	66.27	2.16	7.68	34.02	1.11	3.94
			±6.27	±0.167	±0.687	±4.02	±0.112	±0.942
		10	62.7	2.24	11.94	33.68	1.20	6.41
			±2.72	±0.242	±1.94	±3.68	±0.208	±0.418
		90	66.44	1.90	6.76	31.77	0.91	3.23
			±6.44	±0.904	±0.764	±1.77	±0.917	±0.237
		180	68.17	1.54	3.74	29.40	0.67	1.61
			±8.17	±0.547	±0.747	±9.40	±0.670	±0.610

<sup>a</sup> the relative and absolute contents are on dry basis

**Table 2**

Absolute and relative contents of volatile matter, ash, and fixed carbon in feedstock and biochars prepared at various temperatures and holding times.

	Temperature (°C)	Holding time (min)	Relative content <sup>a</sup>			Absolute content		
			VM (%) <sup>b</sup>	Ash (%)	FC (%) <sup>c</sup>	VM (g)	Ash (g)	FC (g)
Feedstock	-	-	76.00	10.13	13.87	76.00	10.13	13.87
			±2.32	±0.30	±3.87	±2.32	±0.30	±3.87
Biochar		10	39.15	14.18	46.67	27.92	10.11	33.29
			±9.15	±4.11	±6.67	±1.08	±0.36	±1.33

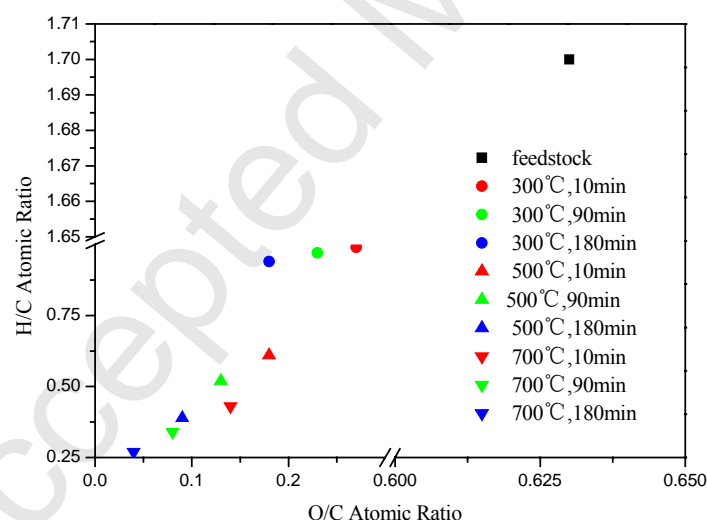
300



500	90	37.67	16.84	45.49	22.57	10.09	27.26
		$\pm 7.67$	$\pm 6.84$	$\pm 5.49$	$\pm 0.89$	$\pm 0.40$	$\pm 0.53$
	180	36.40	18.37	45.23	20.06	10.12	24.92
		$\pm 6.40$	$\pm 8.37$	$\pm 5.23$	$\pm 0.57$	$\pm 0.36$	$\pm 0.86$
	10	23.91	16.45	59.64	14.68	10.10	36.62
		$\pm 3.91$	$\pm 6.45$	$\pm 9.64$	$\pm 0.48$	$\pm 0.42$	$\pm 1.03$
700	90	16.88	17.63	62.49	9.68	10.11	35.82
		$\pm 6.88$	$\pm 0.65$	$\pm 1.83$	$\pm 0.33$	$\pm 0.36$	$\pm 1.02$
	180	14.40	19.66	65.94	7.39	10.09	33.85
		$\pm 0.42$	$\pm 0.70$	$\pm 1.98$	$\pm 0.22$	$\pm 0.36$	$\pm 1.02$
	10	14.47	18.8	66.73	7.77	10.09	35.84
		$\pm 0.43$	$\pm 0.65$	$\pm 2.06$	$\pm 0.23$	$\pm 0.54$	$\pm 1.11$
	90	6.54	21.09	72.37	3.13	10.09	34.61
		$\pm 0.21$	$\pm 0.72$	$\pm 2.23$	$\pm 0.10$	$\pm 0.48$	$\pm 1.07$
	180	6.11	23.42	70.47	2.64	10.08	30.39
		$\pm 0.18$	$\pm 0.73$	$\pm 2.21$	$\pm 0.08$	$\pm 0.31$	$\pm 0.95$

<sup>a</sup> the relative and absolute contents are on dry basis,

<sup>b</sup> VM=volatile matter, <sup>c</sup> FC=fixed carbon,



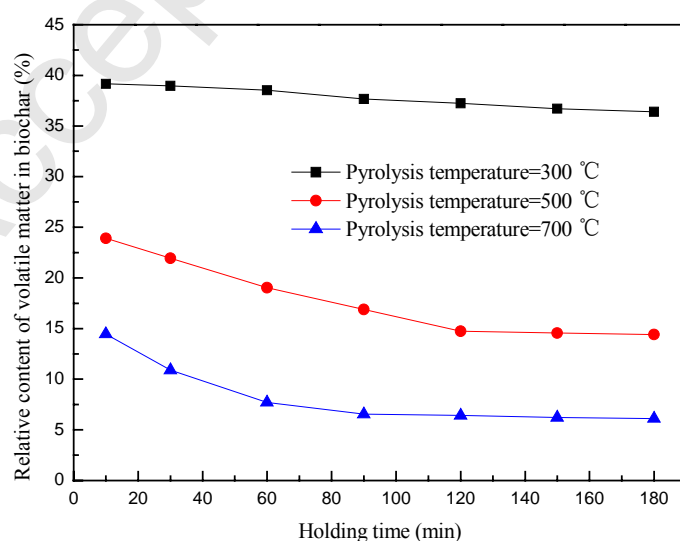
**Fig. 1.** The Van Krevelen diagram for feedstock and biochars prepared with various temperatures and holding time.

### 3.2. Proximate analysis

Without moisture, biochar could be categorized into volatile matter, ash, and fixed carbon according to proximate analysis. Temperature had significant effect on the content of volatile matter. As shown in Table 2, the relative and absolute contents of

volatile matter in biochar were much lower than that in feedstock. In addition, the relative content of volatile matter decreased with temperature rise. In particular, when the holding time was 90 min, the relative content decreased from 47.67% to 6.54% as temperature increased from 300 °C to 700 °C. These results were consistent with previous research findings [7].

Prolonging the holding time could also diminish volatile matter. For detailed exploration, the volatile matter content was measured at 10, 30, 60, 90, 120, 150, 180 min. As showed in Fig. 2, the reduction effect of holding time on volatile matter content was very limited at 300 °C, which just decreased from 39.13% to 36.40% when the holding time increased from 10 min to 180 min. Under high pyrolysis temperature, however, the reduction effect was obvious during the early holding time stage whereas the effect was negligible during the late holding time stage. For example, the volatile matter content decreased quickly from 23.91% at 10 min to 14.73% at 120 min, then decreased slightly to 14.40% at 180 min when the pyrolysis temperature was 500 °C. Under the pyrolysis temperature of 700 °C, the volatile content decreased quickly from 14.47% at 10 min to 7.72% at 60 min, then had minor reduction to 6.11% at 180 min.



**Fig. 2.** The relative content of volatile matter in biochar produced at different pyrolysis temperature and holding time.

As ash was composed of various minerals with good thermostability in the form of oxide, sulfate, phosphate, silicate etc., the absolute content of ash in biochar was stable. The absolute ash content was between 10.08 and 10.12 g, which was consistent with that in feedstock (10.13 g). By contrast, the relative ash content in biochar increased with increasing temperature and extended holding time.

Taking into account of the results that the absolute content of volatile matter in biochar decreased and the relative and absolute content of fixed carbon in biochar increased (Table 2) while the absolute ash content in biochar and feedstock was almost the same, some volatile matter in the feedstock was converted to fixed carbon in biochar during pyrolysis. As volatile matter was easily decomposed with the actions of microorganisms whereas fixed carbon was biologically and chemically recalcitrant [24], the conversion of volatile components to fixed carbon components may be considered as the intrinsic mechanism of biochar carbon sequestration.

### 3.3. Biochar porosity characteristics

Table 3 presents pore structure parameters of the biochars obtained at different temperatures and holding times. The devolatilization of feedstock developed porosity in the biochars, resulting in particles with an essentially micro–macropore structure. It can be observed that the biochar formed at 300 °C and 10 min had the smallest BET surface area and pore volume, and more organic materials cracking. The  $S_{\text{BET}}$ ,  $V_{\text{micro}}$ ,  $V_{\text{meso}}$  and  $V_{\text{total}}$  values increased gradually with increasing temperatures and longer holding time and reached the maxima (11.80 m<sup>2</sup> g<sup>-1</sup>, 0.0058 cm<sup>3</sup> g<sup>-1</sup>, 0.0039 cm<sup>3</sup> g<sup>-1</sup> and 0.0178 cm<sup>3</sup> g<sup>-1</sup>, respectively) at 700 °C and 180 min. Nevertheless, the pore diameter hardly changed during the pyrolysis temperature and holding ranges. As abundant minerals may fill the pores in biochar, this study showed that the pore structure of biochar was poor, which agrees with several previous reports [23, 25]. Although acid washing is an effective approach to develop pore structures, it is

usually not used for biochar because it may remove minerals that are necessary to fertile soil. Furthermore, the filled pores of biochar could have a series of effects on soil properties, specifically, micropores might adsorb nutrients and improve soil fertility [26]; macropores could improve soil aeration, water infiltration [6] and increase soil microbial content through enhancing microorganism survival and propagation by providing suitable shelters [12].

**Table 3**

Characteristics of porosity in biochars derived from pyrolysis at different temperatures and holding time.

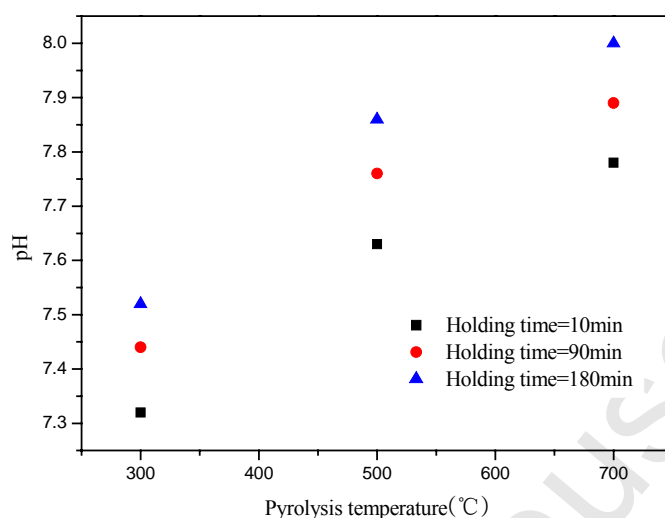
Temperature (°C)	Holding time (min)	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ ) <sup>a</sup>	$V_{\text{micro}}$ ( $\text{cm}^3 \text{g}^{-1}$ ) <sup>b</sup>	$V_{\text{meso}}$ ( $\text{cm}^3 \text{g}^{-1}$ ) <sup>c</sup>	$V_{\text{total}}$ ( $\text{cm}^3 \text{g}^{-1}$ ) <sup>d</sup>	$D_{\text{ave}}$ (nm) <sup>e</sup>
300	10	2.32	0.0012	0.0007	0.0042	38.07
	90	3.78	0.0018	0.0008	0.0053	37.79
	180	4.45	0.0023	0.0010	0.0075	36.70
500	10	3.63	0.0016	0.0011	0.0059	35.67
	90	5.89	0.0026	0.0018	0.0089	36.45
	180	8.50	0.0037	0.0023	0.0125	36.21
700	10	5.57	0.0026	0.0014	0.0094	36.78
	90	8.68	0.0038	0.0028	0.0136	36.48
	180	11.80	0.0058	0.0039	0.0178	37.23

<sup>a</sup>  $S_{\text{BET}}$ , apparent BET area; <sup>b</sup>  $V_{\text{micro}}$ , microporous volume; <sup>c</sup>  $V_{\text{meso}}$ , mesoporous volume; <sup>d</sup>  $V_{\text{total}}$ , total pore volume; <sup>e</sup>  $D_{\text{ave}}$ , average pore diameter.

### 3.4. pH

As shown in Fig. 3, all the biochars were alkaline, with the pH range of 7.3-8.0. The pH value increased with the increasing pyrolysis temperature and holding time. Gaskin et al. [4] reported that biochars generated from poultry litter, peanut hulls, and pine chips through 400 °C pyrolysis had pH values of 10.1, 10.5 and 7.6, respectively. The increase of ash components (Table 2) may account for the increase of biochar pH. Yuan et al. [27] indicated that inorganic carbonates were the major alkaline components of the biochars generated at high temperature, and that organic anions ( $-\text{COO}^-$  and  $-\text{OH}^-$ ) contributed to the alkalinity of biochars generated at low

temperature. However, no obvious difference of the organic anions has been found from our biochars FTIR spectra (Fig. 4 and Fig. 5).



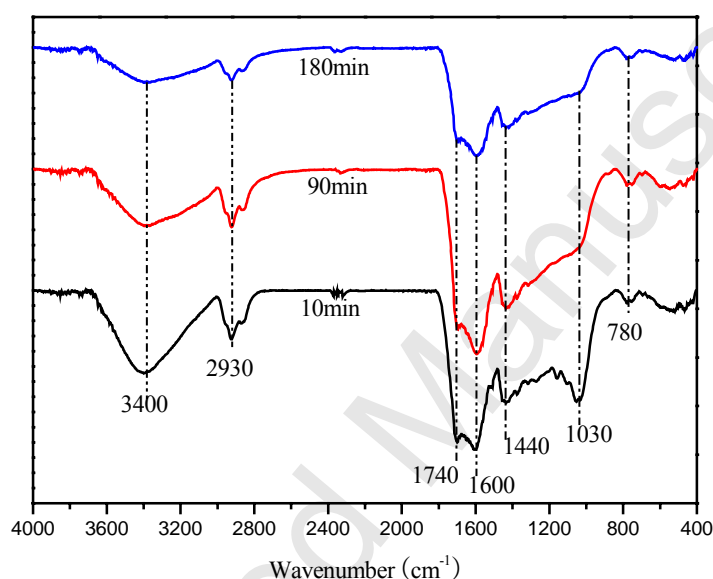
**Fig. 3.** pH of biochars prepared at different pyrolysis temperatures and holding time.

### 3.5. FTIR of biochars

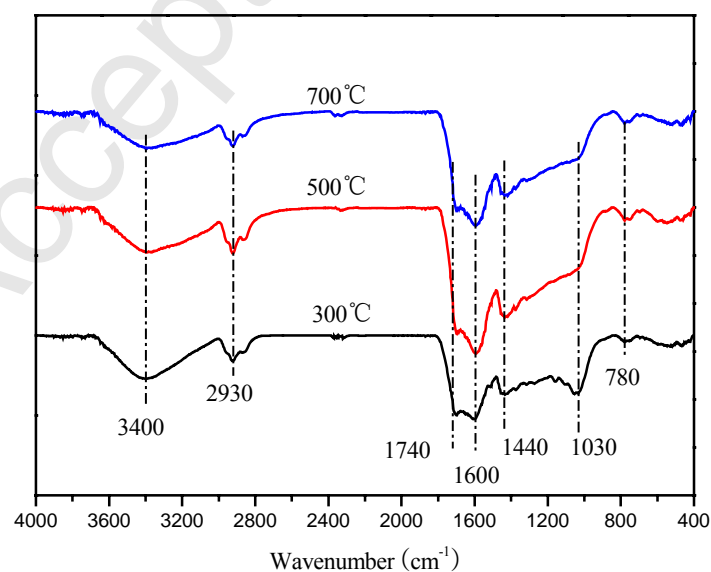
FTIR spectra of the biochars derived under different temperatures at 10 min, and the biochars derived under 700 °C at different holding time were chosen to illustrate the effect of pyrolysis temperature and holding time on their spectral properties, respectively. As presented in Fig. 4 and Fig. 5, the typical spectrum has several absorption bands. The broad band around 3400  $\text{cm}^{-1}$  was assigned to O-H stretching [24, 27], 2930  $\text{cm}^{-1}$  to aliphatic C-H stretching [24, 28], 1740  $\text{cm}^{-1}$  to C=O stretching for carboxyl, aldehyde, ketone and ester [28], 1600  $\text{cm}^{-1}$  to C=C, C=O stretching (aromatic) [28], 1440  $\text{cm}^{-1}$  to aliphatic  $-\text{CH}_3$  stretching [24], 1030  $\text{cm}^{-1}$  to symmetric C-O stretching for cellulose, hemicelluloses and lignin [24] and 780  $\text{cm}^{-1}$  to aromatic C-H stretching [29].

It was shown that the pyrolysis temperature and holding time have similar effects on biochar spectral properties. Absorption intensities at the band 3400  $\text{cm}^{-1}$  decreased with the increasing pyrolysis temperature and holding time, indicating reductions of O and H elements. With the temperature rise or holding time increase, the absorption intensities at 1740  $\text{cm}^{-1}$  became very weak, suggesting the weakness of biochar

surface polarity. The absence of absorption peaks at  $1030\text{ cm}^{-1}$  indicated the massive cracking of cellulose, hemicelluloses and lignin when the temperature increased to  $500\text{ }^{\circ}\text{C}$  or the holding time extended to 90 min. The decreasing absorption intensities at the bands  $2930\text{ cm}^{-1}$  and  $1440\text{ cm}^{-1}$  and increasing absorption intensities at the bands  $1600\text{ cm}^{-1}$  and  $780\text{ cm}^{-1}$  with the increasing temperature and holding time indicates the decrease of aliphatic hydrocarbon and development of aromatic structure.



**Fig. 4.** FTIR spectra of biochars prepared at  $300\text{ }^{\circ}\text{C}$  and various holding time.



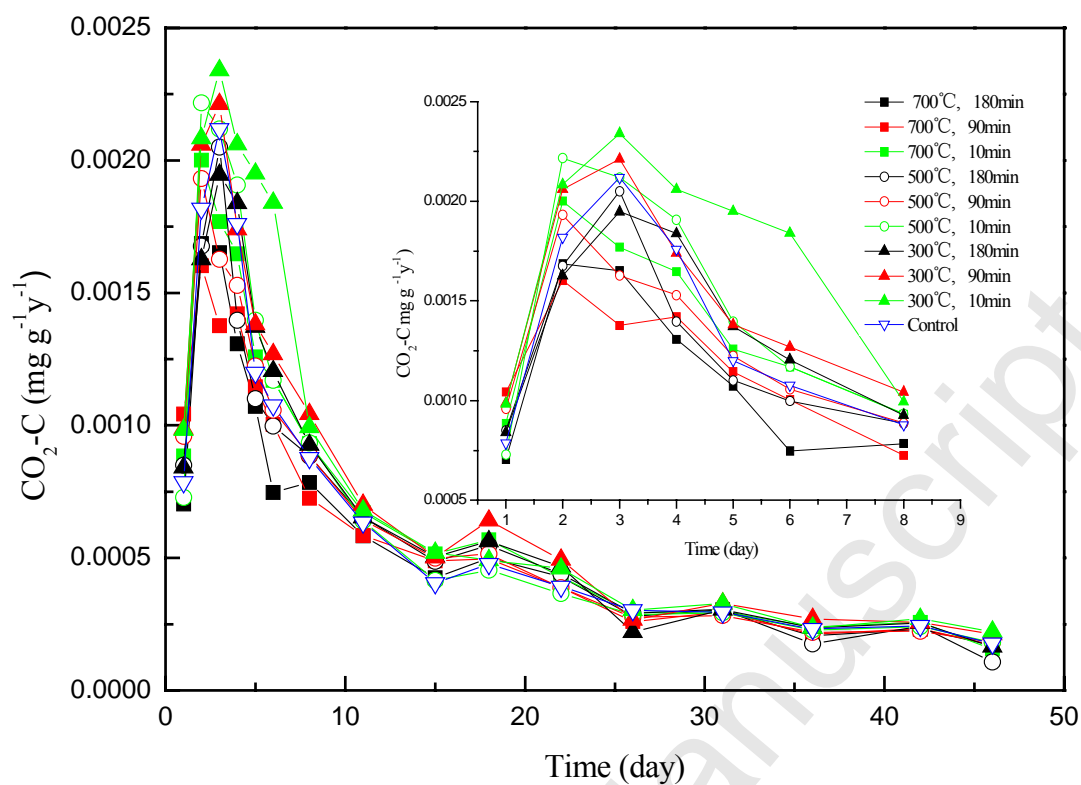
**Fig. 5.** FTIR spectra of biochars prepared at 10 min under different pyrolysis temperatures.

### 3.6. *The energetic sustainability of biochar production*

Unlike other biochar feedstock, the boiled radix isatidis residue has high moisture content. Therefore, the issues of massive energy consumption of biochar production by pyrolysis must be considered. The fresh boiled radix isatidis residue usually contains about 70%-85% water, which could be reduced to 20% using the waste-heat steam for further utilization [30]. As well as energy recovery from sewage sludge pyrolysis [31, 32], the pyrolysis oil and combustible gases derived from pyrolysis of boiled radix isatidis residue could be used as fuels for biochar production. The waste-heat steam, together with the pyrolysis oil and combustible gases could provide a considerable amount of energy for sustaining boiled radix isatidis residue dehydration and biochar production during pyrolysis.

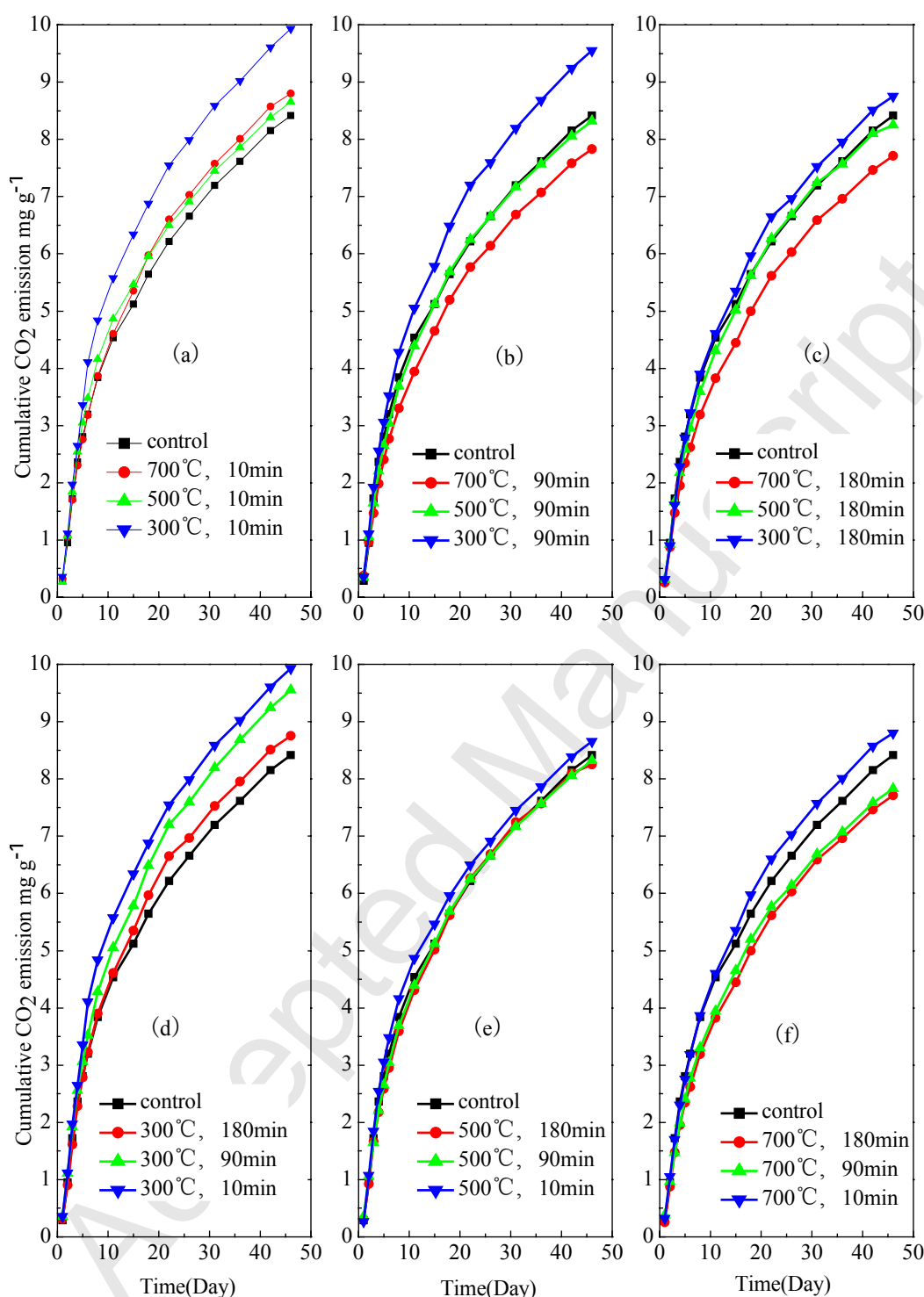
### 3.7. *Soil CO<sub>2</sub> emission*

The CO<sub>2</sub> emission rates of the control sample and soil with various biochars were shown in Fig. 6. The variations of the CO<sub>2</sub> emission rates with incubation time were similar among the samples. Given the dark and short-term experimental incubation conditions, soil microbial activity may be one of the vital factors affecting soil CO<sub>2</sub> emission rates because CO<sub>2</sub> was primarily derived from soil organic carbon and biochar degradation by microorganisms. The soil microbial activity was low on the first day of the incubation as soil was pretreated through air drying. After soil rewetting, soil microbial activity would be enhanced rapidly [33]. Thus, soil CO<sub>2</sub> emission rates dramatically increased to peak on the second or the third day in this study. However, the CO<sub>2</sub> emission rates decreased quickly during the subsequent stage of incubation. Several similar observations have been found during incubations of soil amended with biochar derived from rice straw and oak [24, 34]. From the tenth day onwards, the CO<sub>2</sub> emission rates became lower than that on the first day. The decrease of CO<sub>2</sub> emission rates may be explained by the insufficiency of microbially utilizable carbon and other nutrient sources.



**Fig. 6.** CO<sub>2</sub> emission rates of control and soil with biochar prepared at various temperatures and holding time.





**Fig. 7.** CO<sub>2</sub> cumulative emissions of control and soil with biochar produced at different temperatures and holding time.

The cumulative CO<sub>2</sub> emissions of the control and soils with biochar produced at various temperatures and holding time were shown in Fig. 7. In Fig. 7a, the holding

time was kept constant at 10 min. It is obvious that adding biochar produced at 300 °C could enhance soil cumulative CO<sub>2</sub> emission; however, adding biochar produced from 500 °C and 700 °C did not show much positive effect. As shown in Fig. 7b and Fig. 7c, the holding time was 90 min and 180 min respective. Both adding biochar produced at 300 °C enhanced soil cumulative CO<sub>2</sub> emission, whereas that produced at 700 °C restrained soil cumulative CO<sub>2</sub> emission. The cumulative CO<sub>2</sub> emissions of control and the soil incorporated with biochar produced at 500 °C were almost the same. Fig. 7d shows that adding all the biochar produced at 300 °C could enhance soil cumulative CO<sub>2</sub> emission, but the positive effect was lessened when the added biochar was produced with longer holding time. In Fig. 7e where the pyrolysis temperature was 500 °C, only the biochar produced at 10 min enhanced soil cumulative CO<sub>2</sub> emission. The cumulative CO<sub>2</sub> emissions of soils added with biochar produced at 90 min and 180 min were similar with that of the control. In Fig. 7f where the pyrolysis temperature was 700 °C, the biochar produced at 10 min enhanced cumulative CO<sub>2</sub> emission whereas the added biochar produced at 90 min and 180 min restrained cumulative CO<sub>2</sub> emission.

These results agree with previous observations that biochar may have a positive or negative effect on soil CO<sub>2</sub> emission [35]. The positive effect may lie in a direct mechanism of the increased production of extracellular enzymes because of the addition of biochar which acted as a mineralizable carbon source to “co-metabolize” soil organic matter [36, 37]. Therefore, the soil CO<sub>2</sub> emission was found to be related to volatile matter content in the added biochar. Our results confirmed that biochar produced at 300 °C or 10 min contained more volatile matter (Table 2) and enhanced soil CO<sub>2</sub> emission. In addition, as biochar also contains nitrogen, phosphorous, and other micronutrients, the positive effect might also come from the stimulation of microbial activity through these micronutrients [37]. Other indirect mechanisms, such as the improvement in soil aeration, moisture, or structure [37] were not able to be verified here because of the constant laboratory incubation condition.

Although the biochar produced under two conditions (700 °C/90 min and 700 °C /180 min) contained an amount of volatile matter, the CO<sub>2</sub> emission of the soil

incorporated with biochar was still less than that of the control, suggesting a negative effect of biochar on soil CO<sub>2</sub> emission. As these biochar pH were relatively high (Fig. 3), the results were inconsistent with previous reports that biochar with high pH may enhance soil CO<sub>2</sub> emission through strengthening microbial community respiratory metabolism [38]. The negative effect of biochar may be ascribed to biochar's extensively porous structure, which would adsorb soil organic carbon on its greater surface area and enclose soil organic carbon into its developed micro-pore network to lessen the availability of soil organic carbon [39].

In other words, the actual effect of biochar on soil CO<sub>2</sub> emission lay in the combined actions of biochar properties. For example, biochar produced at 300 °C or 10 min contained a large amount of volatile matter (Table 2), with poor porous network (Table 3) and slight alkalinity (Fig. 3). Thus, the addition of such biochar may enhance soil CO<sub>2</sub> emission. On the other hand, biochar produced at 700 °C, 90 min, or 180 min contained less volatile matter (Table 2), with advanced porous network (Table 3) and strong alkalinity (Fig. 3). Hence, the addition of such biochar may lessen soil CO<sub>2</sub> emission. When there was no change in soil CO<sub>2</sub> emission, it could be implied that the magnitudes of two opposite effects were equal. Furthermore, the effect of biochar on soil CO<sub>2</sub> emission was associated with pyrolysis conditions. Adjusting temperature and holding time may affect biochar properties, including volatile matter composition, porous network and pH, and subsequently govern soil CO<sub>2</sub> emission when biochar was returned to soil as amendment.

To summarize, the effects of biochar on soil CO<sub>2</sub> emission were related with the biochar type, soil type, and incubation condition. Our results only reflect the effect of biochar produced under experiment conditions on soil in southern China, which may not be generalizable to other types of biochar on different soil source and/or experiment conditions. However, a negative effect was more likely to occur when biochar returned to soil was produced at a higher temperature and longer holding time.

#### 4. Conclusions

Pyrolysis temperature and holding time had significant effects on properties of biochar derived from boiled radix isatidis residue. Increasing temperature and extending holding time may reduce the volatile matter content, enhance carbon enrichment, and develop aromatic structure in biochar, producing alkaline biochar with weak surface polarity, high specific surface area and extensively porous structure. The effect of biochar on CO<sub>2</sub> emission of soil in southern China lays in biochar properties, especially of volatile matter content, porous structure and pH. Increasing temperature and extending holding time may convert the positive effect into a negative effect then to reduce soil CO<sub>2</sub> emission. Taking into account of the differences of incubation experiment and actual soil conditions, farm tests must be conducted further to verify the effect of biochar derived from Radix isatidis on soil CO<sub>2</sub> emission.

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**Highlights**

1. Boiled radix isatidis residue was used for biochar production.

2. Pyrolysis temperature and holding time affect biochar properties.

3. Biochar properties affect soil CO<sub>2</sub> emission.

4. Increasing temperature may restrain soil CO<sub>2</sub> emission.

5. Prolonging holding time may restrain soil CO<sub>2</sub> emission.